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## OXIDE CERAMIC SINTERING PARTICULARS

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The sintering of intermediate powder articles based on oxide ceramic is examined from the standpoint of diffusion mass transfer. Two types of powders, differing by the preparation methods, are used in practice. As a rule, the more coarse powder is usually obtained by mechanical comminution while the other powder, characterized by a high dispersity and content of different types of crystal lattice defects in the particles, is obtained by chemical methods, such as precipitation from solutions, heterophase interaction, cryo- and plasma-chemical treatment, and so forth. It is shown that when intermediate articles are sintered they are compacted and hardened by different physical mechanisms.

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**Key words:** sintering, diffusion, crystal lattice defects, powder dispersity, sintering mechanism.

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Sintering is understood to mean the totality of the processes which occur when an intermediate powder part is heated and transform the part into a monolithic state. The foundations of our modern understanding of the physical nature of the phenomena were laid in the middle of the last century. Ya. I. Frenkel developed the idea that the driving force for the spontaneous compaction of a porous body, i.e., its deformation, is the tendency for the free surface area to decrease, the kinetics of the process being determined by the laws of viscous flow (creep) of the material [1]. The force giving rise to the compaction was also identified — surface tension (Laplace capillary pressure). B. Ya. Pines [2] discovered the physical mechanism responsible for the filling of pores: vacancy-wise evaporation of a pore as a “drop of void” in a crystal followed by the diffusion of vacancies toward sinks — the boundaries and exterior surface of the body. This is due to the presence of a vacancy concentration gradient above sections of the surface with different curvature.

For the exposition given below, it is important to call attention to the particulars of the creep deformation processes occurring in different solid bodies. Similarly to liquids, amorphous bodies exhibit viscous flow comprising a cooperative motion of a group of atoms occurring by means of displacement and rotation. The chemical bonds in them are

spherically symmetric, i.e., all bonds are equivalent and during deformation the adjustment of micro- and macrovolumes of the body proceeds unimpeded. As a crystal lattice forms, a predominant direction for the bonds, and thereby the reason for the orientation of the motion of separate elements, appear.

Metal lattices are quite simple and cooperative transformations of their elements in definite crystallographic directions are possible by means of displacement and rotation over a short distance (less than the interplanar separation). Plastic flow in a material consists of the displacement of dislocations, boundaries of blocks and crystals, as well as other lattice defects.

Cooperative motion is virtually excluded in the complex lattice of a ceramic consisting of several sublattices. Only diffusion of ions differing by kind, size, as well as the magnitude and sign of the charge and possessing rigidly directed, strong ionic-covalent bonds is possible — diffusive-viscous flow. At the same time an adjustment mechanism in individual sections of a structure, similar to cooperative transport — flow, including also coalescence, plays a definite role in fine-crystalline objects, having a high density of defects, smaller than 1  $\mu\text{m}$  and the main role in objects smaller than 0.1  $\mu\text{m}$  [3].

It is significant that an entire collection of defects at every structural level (macro-, micro-, and sub-structure) is present in real crystals and every defect possesses its own energy [4]. In other words, depending on the crystal-chemical

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structural particulars and the preceding technological processing a material is characterized by a spectrum of states of its structural elements each having a definite energy distribution. Since the behavior of all defects as a whole determines the deformation of a body, the action of any one mechanism (i.e., the effect of one type of defect) can be observed only in special experiments. The deformation of real powder or compacted materials is determined by a complicated combination of elementary processes, and ordinarily only wide transitional (mixed) regions are observed.

To fabricate ceramic by sintering powders we employ a characteristic feature of solid bodies, namely, their high inertia in all interaction processes, specifically, the high (higher by many orders of magnitude) viscosity under normal conditions as compared with liquid and gaseous bodies. The result is that there is not enough time for them to dissipate (disperse) the energy supplied to them in fast, nonequilibrium, and irreversible processes. The accumulated energy can be dissipated if the viscosity of the object decreases, i.e., if the mobility of the constituent elements increases, for example, with thermal activation. Just such a possibility is indicated by the Clausius–Clapeyron equation state  $(p\nu)/T = \text{const}$ , where the constant has the dimensions J/K. It is technically difficult to change the product  $(p\nu)$ ; ordinarily, the processes are conducted under isobaric conditions where a thermal change of volume is observed if an energy unbalance is present. An example of such excess energy is the driving force for “spontaneous”<sup>3</sup> sintering.

In present practice, mainly two methods are used to obtain powder materials — mechanical dispersion and chemical methods. Comparatively large particles are ordinarily obtained in the first case and much smaller particles in the second case. Actually, the powders obtained by both methods are a metastable state of particles whose free energy is elevated. This is also manifested as a high sorption capacity of particles for gases and radicals and the capability of consolidation (compaction) with time as well as aggregation during the production processes.

The existing data show that grinding can produce powders with particle sizes of the order of a micron and larger [5]. Ordinarily, further comminution practically ceases; only some amorphization of the surface layers of the particles and the destruction of their lattice regularity as a result of the formation of defects — stress concentrators — are observed. It is assumed that in this case energy is accumulated as a result of the appearance of new separation boundaries and lattice defects, i.e., it is stored in the form of the excess energy of defects — vacancies, dislocations, boundaries of blocks and crystals, amorphized sections of the volume — as well as the energy of new internal and external surfaces.

The principal feature of particles obtained by mechanical dispersal is as follows. Ordinarily, particles retain a crystal lattice, though very high degrees of lattice distortion, right up

to the formation of amorphized layers at the surface, can be reached. The material particles in a compact made from ground powders are removed from the state of equilibrium because of the extended nature of the free surface and because of the presence of excess vacancies, stacking faults, dislocations, cracks, pores, and so on. Some authors consider such pores to be “active,” even though this concept remains indeterminate; powders sintering more rapidly and better at lower temperatures as compared with other powders are said to be active; the activity is assumed to be due to precisely the defects and the mechanical stresses associated with them.

A characteristic feature of the chemical methods of obtaining powders by means of reactions in solutions of liquids, heterophase interactions, and so on is that they are conducted under conditions far from equilibrium [6, 7]. As a result, new embryo growth actually stops at the crystal nucleation stage and highly dispersed particles with high defect density, size of the order of nanometers, and highly extended inner and outer surfaces are obtained. Their shape is rounded and crystal structure strongly distorted — x-ray amorphous. All this can be interpreted as the creation of accumulating structures by the system of particles.

Practice shows that the highly disperse oxide powders obtained by modern chemical technologies are very active to sintering. Ordinarily, the dispersity of such powders is briefly characterized as “less than a micron,” i.e., it lies in the nanometer size range. As a rule, the particles are comparatively large aggregates, of the order of ten nanometers, consisting of fine particles bound together by adhesion forces [8]; the aggregation is due to the overlapping of partially compensated bonds of surface atoms. The formation of a large number of surface defects — vacancies, dislocations — is characteristic for particles of this size.

When a solid particle appears under strongly nonequilibrium conditions, the overlapping of the chemical bonds of neighboring atoms occurs randomly, in a disordered fashion, loosely and a large number of structural imperfections of different kinds are formed. In addition, the distribution of defects over the cross section of the particles is nonuniform: their concentration is higher at the surface. For this reason, on the basis of the simplest ideas it can be assumed that as the dispersity increases, the near-surface layer plays an increasingly larger role, since the fraction of this layer in the volume increases. For example, corundum particles (i.e.,  $\alpha\text{-Al}_2\text{O}_3$ , crystal lattice parameter  $c \approx 1.3$  nm) with specific surface area  $100 \text{ m}^2/\text{g}$  (BET method) have surface-averaged diameter  $0.015 \mu\text{m} = 15 \text{ nm}$ , i.e., ten unit cells fit along it. Therefore, the state of the atoms which comprise the particle is closer to a surface than volume state. The surface-averaged particle diameter for specific surface area  $10 \text{ m}^2/\text{g}$  is  $150 \text{ nm}$ , which fits 100 cells; in general, their state is intermediate between a surface and volume state. It should be kept in mind that the surface of such particles is qualitatively different from that of larger particles, since they are comprised of atoms with partially compensated chemical bonds

<sup>3</sup> This term is obsolete and unfortunate, since a completely definite driving force exists and there is no arbitrariness.

and the sites surrounding them in a cell are not completely filled. As a result of the high nonuniformity of the process forming a new phase, the powder particles have a rounded shape with fractal surface structure and a strongly distorted crystal structure [9, 10].

Another aspect of such a state manifests as the appearance of large hydrostatic compression forces in finely dispersed particles as a result of an increase of the surface tension. For example, for approximately 1  $\mu\text{m}$  size these forces are approximately 0.5 MPa and increase with the dispersity of the powder. The enormous compressive surface-tension forces in nanoparticles are one reason for the unstable state of the body; another reason is a very high concentration of imperfections. All this changes the character of the material. For example, as compared with the monolith, the melting temperature of such powder decreases appreciably during heating [3].

Summarizing, it must be underscored that two types of imperfections (defects) responsible for the high energy of the particles are characteristic for nanometer-size particles. The first type, also characteristic of the large objects studied above, are displacements of atoms (ions) from their regular positions (vacancies, dislocations, and so on) and are related with the presence of local mechanical stresses or surface sections with nonzero curvature. The second type, which are characteristic only for nanosize particles and are actually atoms (ions) with uncompensated chemical bonds because of their position on steps, ledges, and corners of small particles, are only negligible large than a unit cell. It can be said that in these two cases the excess energy is determined by different forces: mechanical stresses or chemical affinity.

Thus, it can be assumed that there exist two size ranges of powder particles where considerably different mechanisms of accumulation of energy by them exist. The boundary between them can be defined conventionally as separating the micro- and nanometer measurement ranges. Judging from the data obtained, this boundary lies roughly near 1  $\mu\text{m}$ . It is bounded by wide transition zones of approximately an order of magnitude on either side. It is remarkable that according to an estimate by B. B. Kadomtsev [11] the boundary between the macroworld, where the laws of classical mechanics operate, and the microworld, where the laws of quantum mechanics operate with the wave description of particles, lies in this region — near  $10^{-5}$  cm.

Powders with particles larger than 1  $\mu\text{m}$  accumulate energy in the form of free surfaces with nonzero curvature and in the form of the energy of crystal lattice defects. For powders with particles smaller than 1  $\mu\text{m}$  an increase of the energy of atoms (ions) with uncompensated chemical bonds, located on surfaces, steps, ledges, and corners of nanosize particles, are added to this. It is important that the state of such atoms is close to a surface state, so that the formation energy of the corresponding vacancies by means of quasichemical reactions is close to the formation energy of surface vacancies [12].

We note that both mechanisms of accumulating energy actually represent a change in the state of the chemical bonds, specifically, their distortion by mechanical stresses, partial compensation with formation of new surfaces, ledges, and so on, i.e., further distortion of the lattice right up to amorphization with transition to very fine particles of the order of tens of nanometers. The formation of vacancies with the introduction of additives into the lattice also increases its internal energy as a result of bond distortion.

As a rule, the x-ray diffraction patterns of highly disperse powders carry no information on their crystalline structure. For this reason, such powders are said to be x-ray amorphous. Assuming an x-ray diffraction pattern to be a picture of the diffraction of x-rays by the crystal lattice, one must conclude that in this case we obtain a state called amorphous. This state is characterized by the presence of short-range order only and spherically symmetric bonds without any preferential directions being introduced. Therefore, particles of such sizes tend to acquire the shape of a drop of liquid. In addition, amorphous particles must behave viscously, similarly to drops of liquid, and they must adjust to one another easily — coalesce; the strong surface tension forces promote this. Such a state of the particles affects their behavior during sintering when heated.

It can be imagined that as they continue to grow, small “drops” which have coalesced will manifest the properties of crystals, i.e., definite directions of the forces due to chemical bonds will arise in them, and in the total force field they will not be distinguished sharply from individual particles — the field orients them. Correspondingly, the neighboring large particles likewise are not strongly disoriented, which gives “crystals” the possibility to grow in size by adjusting without mass transfer over appreciable distances. The stronger force field of the crystal lattice contributes to this. It should be noted that such a phenomenon can be observed only in quite pure crystals of compounds or solid solutions, since impurity segregation on boundaries impedes adjustment.

The differences in the states of the two powder types singled out above determine their behavior during sintering. We shall briefly examine the particulars of the mechanisms leading to the intensification (activation) of their sintering processes, having in mind the diffusion-viscous flow model. The flow of an amorphous body can also be studied from these viewpoints, provided that the body is represented as a strongly disordered crystal. On the basis of the concepts expounded above, the origin of vacancies is irrelevant during the formation of a crystal — all vacancies are equivalent. For this reason we shall take the diffusion coefficient  $D$  to be the product  $D \sim n\mu$ , where  $n$  is the concentration and  $\mu$  the mobility of the vacancies. The mobility is structure sensitive. Vacancy motion proceeds by a simpler diffusion path, the rate of displacement of vacancies increases in the order volume — dislocation — boundary — inner surface — outer surface. Thus, a vacancy moves along sites with weakened

chemical bonds, and for solids the process consumes accumulated energy.

The vacancy concentration is determined by activation mechanisms, i.e., vacancy formation, proceeding as a result of energy flowing in or accumulated by the body. The analysis shows that an effective factor which permits changing the concentration reversibly but only within small limits is thermal activation (i.e., heating).

The sources of accumulated energy (lattice deformation and defects, partially compensated chemical bonds) supply appreciably more vacancies but they are irreparable and become exhausted with time. A special case is vacancy formation and lattice deformations accompanying the introduction of foreign atoms: the excess energy of partially realized chemical affinity maintains a constant concentration of point defects.

Thus, two different sintering mechanisms due to the presence of lattice distortions can be imagined.

The first sintering mechanism is diffusion-viscous flow and is due to the presence of vacancy flow from sources to sinks in the force field due to surface tension in the presence of surface sections with nonzero curvature. Here the model of two coalescing particles is fully applicable, their point of contact being stationary, while shrinkage is a consequence of atom-wise displacement of matter to it [3]. The rate of the process is set by the effective diffusion coefficient, which is determined by the vacancy concentration and mobility.

The number of vacancies is determined by different sources (thermal, impurity, non-stoichiometric), their origin being irrelevant for diffusion in a crystal, and they all participate in mass transfer [12]. Vacancy mobility is determined by the form of the path along which a vacancy in a crystal emerges at the surface of a polycrystalline body, i.e., the type of lattice defect which facilitates vacancy motion (dislocation, boundary, surface). Thus, vacancy mobility carries the structurally sensitive part of the diffusion coefficient.

The second mechanism of sintering is characteristic mainly for chemically produced powders which are highly disperse and have a high density of defects. The driving force for the sintering mechanism is the same — surface tension, and its mechanism is the same — diffusive-viscous flow. Added to this is the mechanism by which a highly porous, visco-solid, high-defect body (actually an amorphous body), for which the position of the interparticle contact points is immaterial, undergoes deformation as a unit. The sintering mechanism is realized by adjustment via the displacement and rotation of atoms (ions) over a distance of the order of one unit cell (i.e., by simple restructuring of the bonds in layers near boundaries), the result of which is coalescence of neighboring crystals (particles). A high density of defects, where the state of the particles is closer to being amorphous than to crystalline, makes this possible. In addition, the atoms (ions) comprising a particle possess a high energy, making them close to surface atoms. Actually, the body in this case is a viscous-flow system consisting of fine particles and pores of nanometer size that deforms as a unit.

Since there are qualitative differences between the macro- and micro- states of particles in the two size ranges indicated above, diffusion mass transfer during sintering of the particles sometime proceeds partly by different mechanisms. Large particles harden and compact by diffusive-viscous flow. Vacancy sources and sinks change at different stages, and their diffusion path along the surfaces of pores, boundaries, and volume of crystals thereby also changes [3]. The rate of the process is limited by the surface, boundary, or volume diffusion coefficients. At the same time, at an early stage of the sintering process (after the particles have coalesced) the intermediate part is a single, high-porosity medium consisting of fine pores and particles. Viscous flow under surface tension forces occurs in the intermediate part and the part deforms as a unit, which explains the high shrinkage rate [3]. At the final stage, where pores do not interfere with the motion of boundaries, crystals grow and, as a rule, pores increase in size with practically no decrease in their volume. In the best case, the porosity decreases to 2–3%, and the strength, electrophysical, and other properties of the parts are deficient.

During sintering an intermediate part comprised of highly disperse powder deforms practically as a defective matrix where the state of the atoms is closer to their state on the surface than in the volume of the material. The chemical bonds are only partially compensated. The tight network of short boundaries between fine particles does not permit crystal growth processes to develop, while numerous fine pores are effective obstacles to the motion of boundaries as a unit (here, probably, one can talk about slippage by a diffusive-viscous mechanism). The particles move conservatively by means of displacement and rotation during adjustment. In the process, pores do not collapse in the matrix but rather “float upwards” (as in a liquid) by diffusion. Crystal growth as such occurs only for low values of the porosity and for pore sizes less than the critical value (i.e., they become overgrown). As a result the ceramic reaches a pore-free, transparent state.

Apparently, nanosize powders exhibit special behavior. Here one must talk not about atoms on a surface but rather the surface state of atoms or the surface state of the material — such atoms have a low Fermi level. The state of highly disperse powders is inherited in some way by a fine-crystal ceramic made on their basis, specifically, its structure is looser. This is manifested, specifically, as a decrease of its microhardness, index of refraction, and melting temperature [13, 14].

Highly disperse intermediate parts consist of a fine-crystalline high-porosity medium with inclusions of fine pores, which deforms very slowly. This is determined by the high surface curvature of the particles, which is inversely proportional to their radius. The fractal surface of particles is much extended and is subjected to large forces, determined by the product of the surface tension and specific surface area. All this is reason for the formation of high local supersaturation of vacancies, which in turn possess high mobility along the



surface of particles. Most likely, the body should be regarded as a unit. Thus, three-dimensional models of deformation can be used to a first approximation, though all characteristics of the vacancies must be surface characteristics (concentration, mobility). True, in this case the qualitatively different state of the particles and boundaries between them, which affects their behavior, is not adequately taken into account. Specifically, crystal boundaries cannot detach in the process of crystal growth from such small pores with a large surface curvature.

In summary, for particles in oxide powders there are two size ranges where different dominating mechanisms operate. The boundaries between these regions can be set roughly near 1  $\mu\text{m}$  with 0.1 – 10  $\mu\text{m}$  bordering transition zones. The diffusive-viscous flow mechanism, where matter moves along vacancies from a vacancy source to a vacancy sink, operates in the comparatively coarse-grain first region. A contact point between particles serves as a source while a convex surface of a particle outside a contact serves as a sink. The mechanism of viscous deformation of a porous defective matrix as a unit, where the state of the atoms is closer to their state on the surface rather than in the volume of a particle, operates in the second region. The position of the contact points in this case is irrelevant and particles move by displacement and rotation as they adjust; the pores in such a matrix “float upwards” (as in a liquid) by diffusion.

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